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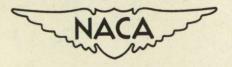
TECHNICAL NOTE 1914

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OXIDATION OF TITANIUM CARBIDE BASE CERAMALS
CONTAINING MOLYBDENUM, TUNGSTEN, AND COBALT

By M. J. Whitman and A. J. Repko

Lewis Flight Propulsion Laboratory Cleveland, Ohio



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OXIDATION OF TITANIUM CARBIDE BASE CERAMALS

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SUMMARY

A number of titanium carbide base ceramals were investigated to determine the oxidation-penetration characteristics at various temperatures and exposure periods. Specimens of the various ceramals, which were composed of titanium carbide and 5, 10, 20, and 30 percent of molybdenum, tungsten, or cobalt, were oxidized in an air atmosphere at temperatures of 1625°, 1785°, and 2000° F. A direct-measurement metallographic method was used to determine the depth of oxidation penetration. A metallographic study was made of the oxidation interface and the oxygen-diffusion zone.

With respect to oxidation penetration, the ceramals containing molybdenum were poorest and the tungsten and cobalt ceramals were about equal in the time-temperature range for which the data were comparable. The oxides formed on the molybdenum ceramals had no protective value in inhibiting further oxidation, whereas the oxides formed on the tungsten and cobalt ceramals had protective properties. The cobalt ceramals were considered more resistant to over-all oxidation than the tungsten ceramals because of their complex, tightly adherent oxide coating.

The depth of oxide penetration in the temperature range of 1625° to 2000° F with varying compositions up to 30-percent molybdenum, tungsten, or cobalt may be estimated from the oxidation-penetration-time curves.

INTRODUCTION

The demand for materials that will possess desirable properties at elevated temperatures has resulted in the development of a group of ceramic-metal mixtures known as ceramals. These materials combine the excellent refractory characteristics of ceramics with the strength and high-melting-point characteristics of certain metallic elements. The ceramals have high strength-to-weight ratios (reference 1) and most of the ceramics considered for use in ceramals are easily obtained.

Carbide base ceramals are receiving particular attention for gasturbine application because they possess strength at elevated temperatures and high thermal conductivity. The high thermal conductivity is valuable in dissipating heat and is also a factor that contributes to good thermal-shock resistance.

If materials are to be suitable for use as gas-turbine blades, they must also have the capacity to withstand the corrosive effects of an air-rich atmosphere at elevated temperature. Quasi-service evaluations of turbosupercharger blades of a titanium carbide - cobalt ceramal indicate that this material has many desirable high-temperature properties but lacks resistance to oxidation (reference 2).

The research reported herein was conducted at the NACA Lewis laboratory to determine the relative resistance to oxidation in an air atmosphere of a group of titanium carbide base ceramals at 1625°, 1785°, and 2000° F and to investigate the types of coating formed. Twelve compositions were investigated: 5, 10, 20, and 30 percent of the elements, molybdenum, tungsten, or cobalt, with the balance of all ceramals consisting of titanium carbide. The ceramals are hereinafter designated only by the metallic constituent.

The results presented include the oxidation penetration during various periods of time, the effect of temperature on oxidation penetration, and the effect of change in composition on oxidation penetration. The relative merits of molybdenum, tungsten, and cobalt as addition elements with regard to oxidation resistance are evaluated within the temperature range covered. Plots of oxidation-rate constant against reciprocal of absolute temperature are presented as an aid in estimating the oxidation penetration of the various materials that will result from exposure to air atmospheres at temperatures between 1625° and 2000° F.

Metallographic examinations of the oxide coatings were made to reveal differences in the oxidation mechanism for the three metallic addition elements. Comparisons were made of the tenacity of the oxides to the ceramals.

The materials were fabricated by Kennametal, Inc. by cold-pressing fine powder into 1/4-by-1/2-by-4-inch bars that were then sintered at suitable temperatures in a controlled atmosphere.

MATERIALS, APPARATUS, AND PROCEDURE

The ceramal specimens used in the oxidation determinations were taken from specimens that had been subjected to a 1600° F modulus-of-rupture test in a helium atmosphere. The compositions investigated

consisted of a titanium carbide base material alloyed with 5, 10, 20, or 30 percent of cobalt, tungsten, or molybdenum. Chemical analyses of the ceramal compositions investigated showed the presence of approximately 6-percent additional tungsten in the form of tungsten carbide in molybdenum and tungsten ceramals (reference 1). In the cobalt ceramals, this contamination is usually less than 1 percent and the highest percentage analyzed was 2.1 percent of tungsten. The presence of the tungsten carbide was probably due to pickup during milling in ball mills using tungsten carbide balls.

Oxidation specimens were prepared by sectioning the modulus-of-rupture bars into 1/4-by-1/4-by-1/2-inch rectangular prisms. The faces were so ground that two opposite surfaces (reference faces) were parallel within ± 0.0001 inch. The distance between reference faces was measured before the oxidation exposure with an accuracy of ± 0.0001 inch.

A resistance furnace with silicon carbide heating elements was used to oxidize the specimens in an air atmosphere at temperatures of 1625° , 1785° , and 2000° F. Temperatures controlled by a potentiometer were held to a maximum deviation of $\pm 15^{\circ}$ F. The temperature was checked by means of two chromel-alumel thermocouples placed in the specimen heating zone.

After the oxidation period, the oxide coating formed was carefully ground from a surface perpendicular to the reference surfaces. During grinding, observations were made of the relative resistance of the oxide to grinding, the adherence of the oxide to the specimen, and the presence or absence of striation.

After a specimen was ground, the unoxidized cross section of the material was measured by means of a calibrated microscope stage and the reticle of a filar eyepiece with an accuracy of ±0.0004 inch. The dimensions of the unoxidized area were measured at six points, three evenly spaced along the length and three along the width, and the decrease from the original dimensions averaged for the six measurements. The microscopic-measurement technique was used because even penetration of the oxide formed an easily visible line of demarcation between the unoxidized area and the oxide coating. Change in specimen weight during oxidation was considered an inaccurate indication of the amount of oxidation because an oxide formed on the molybdenum-ceramal specimens was observed to sublime at elevated temperatures.

Representative specimens were mounted in bakelite and polished for metallographic examination of the ceramal, the oxidation interface, and the oxide over a range of magnification both in the etched and unetched condition.

In order to determine the oxide compositions, the oxidized surfaces were scraped to provide powders for use in X-ray-diffraction analysis. Analyses were made of oxide samples taken at different depths through the oxide layer in an attempt to determine changes in composition within the oxidation layer.

RESULTS AND DISCUSSION

Oxide Penetration

The results of the oxidation determinations are presented in figures 1 to 6 as plots of depth of oxidation penetration plotted against oxidation time, slope of the penetration-time curve (herein-after called oxidation-rate constant) plotted against the reciprocal of the absolute temperature, and oxidation-rate constant plotted against percentage of molybdenum. Instead of fairing in the lines by the method of least squares, all experimental factors were considered and points judged most reliable were given the greatest weight. The contaminant, tungsten carbide, introduced during fabrication probably is a contributing factor, with other processing variables, to the scatter of data points evident in figures 1, 4, and 6. The small and variable percentage of tungsten carbide precludes any attempt to determine the effect of the tungsten carbide present on the oxidation penetration or oxidation mechanism.

The oxidation-penetration - time curves for molybdenum ceramals are presented in figure 1. Figure 1(b) is an enlarged view of the area on figure 1(a) bounded by the origin, 0.02-inch penetration, and 18 hours. The depth of oxidation of these materials increases linearly with time, which indicates that the coating formed during oxidation does not slow the diffusion of oxygen to the oxidation interface. Increasing the percentage of molybdenum has a marked detrimental effect on the oxidation resistance.

The effect of change in temperature on the oxidation rate of molybdenum ceramals agrees well with the exponential formula $K = e^{A/T}$ (where K is the slope of the oxidation-penetration - time curve hereinafter designated the oxidation-rate constant, T is the absolute temperature, and A is a constant). For the molybdenum ceramals $K = \Delta p/\Delta t$, for the tungsten ceramals $K = \Delta p/\Delta \log t$, and for the cobalt ceramals $K = \Delta \log p/\Delta \log t$, (where p is oxide penetration in in. and t is time in hr). The numerical values of K cannot be used as a basis for comparing molybdenum, tungsten, and cobalt ceramals.

The agreement is satisfactory for all the molybdenum ceramals at 2000° and 1785° F and for the 5- and 10-percent molybdenum ceramals at 1625° F. The oxidation rate of the 20- and 30-percent molybdenum ceramals at 1625° F is lower than would exist if the rate formula held consistently. The curves are assumed to be consistent with the oxidation-rate formula at the higher temperatures because of the parallelism of the curves representing various molybdenum contents (fig. 2). Figure 2 indicates that at 1785° F and at 2000° F increasing the percentage of molybdenum results in a drastic increase in oxidation-rate constant. The variation in oxidation-rate constant at 2000° F caused by variation in the percentage of molybdenum is shown in figure 3.

The oxidation-penetration-time characteristics of the tungsten ceramals are presented in figure 4. The data may be presented as a series of straight lines if plotted with oxidation penetration on a linear scale and the time of oxidation on a logarithmic scale. Because the use of semilog paper results in straight lines, the oxidation product formed on the tungsten ceramals evidently has a better resistance to oxygen diffusion than that found on the molybdenum ceramal.

In general, the ceramals containing the high percentages of tungsten had low resistances to oxidation (fig. 4(d)). At a temperature of 1625° F, the 20- and 30-percent-tungsten ceramals oxidized much more rapidly than the 5- and 10-percent-tungsten ceramals but at 2000° F the oxidation-penetration rates of the tungsten ceramals were of the same order of magnitude.

An appreciable increase in oxidation-rate constant at a temperature of 1625° F when the tungsten percentage is increased from 10 to 20 percent is shown in figure 5. At 1785° F, the oxidation-rate constants for the 20- and 30-percent-tungsten ceramals are less than at 1625° F whereas the oxidation-rate constants of the 5- and 10-percent tungsten ceramals remain practically constant. At 2000° F, the oxidation-rate constants for all tungsten compositions are higher than for the two low temperatures investigated.

The nonconformity of the oxidation-rate constants of the tungsten ceramals to the exponential rate formula indicates a possible change in oxidation mechanism as temperature and percentage of tungsten vary.

The oxidation-penetration and time data for the cobalt ceramals are presented in figure 6. The generation of straight lines with slopes less than 1 on log-log coordinates indicates that the scale

formed is protective and inhibits further oxidation (reference 3). The effect of increasing the percentage of the metallic component is not as harmful to the oxidation resistance of the cobalt ceramals as it is to either the molybdenum or the tungsten ceramals.

The oxidation-rate constants for the cobalt ceramals appear to be practically independent of temperature at the three temperatures considered (fig. 7). At 1625° F, the oxidation-rate constant of the 30-percent-cobalt ceramal was found to be higher than for any of the other temperature-composition combinations.

Examination of Oxidation Zone

The phenomenon of surface oxidation is dependent upon the rate at which oxygen for the oxidation reaction reaches the oxidation interface. If the oxide formed offers no resistance to diffusion of the oxygen, the thickness of the coating will increase linearly with time. If the oxide formed is tightly adherent and resistant to the diffusion of oxygen, the rate of oxidation will decrease as the thickness of the oxide increases. If the oxide formed is volatile at the oxidation temperature, it will leave the surface and afford no protection; whereas at the same temperature another oxide may be close enough to the melting point to sinter and form a very dense protective coating. Another factor important in determining whether or not an oxide will have protective properties is its specific molecular volume. The specific molecular volume is defined as the volume of l gram mole of solid at room temperature. The oxides that have a specific molecular volume slightly greater than the unoxidized metal will form dense protective coatings (reference 3). If the specific molecular volume of the oxide is large compared with that of the unoxidized material, however, the oxide will break away at the oxidation interface and will have no protective value.

Examination revealed that the oxide coatings of the molybdenum ceramals were rather chalky and porous. The oxidation penetration into all the molybdenum ceramals was along an interface parallel to the surface at all temperatures investigated. The oxides formed on the tungsten ceramals were somewhat more adherent and were harder to remove by grinding than the oxides formed on the molybdenum ceramals. With the exception of the 20- and 30-percent-tungsten ceramals at 1625° and 1785° F, the oxidation penetration of the tungsten ceramals moved along linear fronts. Oxidation penetration took place along grain boundaries in the excepted cases with the grain-boundary penetration very slight at 1625° F as compared with that at 1785° F.

The oxide coating formed on the cobalt ceramals was found to be very hard and tightly adherent. The coating forms along an interface parallel to the surface and some tendency exists for the coating to chip along a plane within the oxide layer. The coating on the cobalt ceramals is more complex than that found on the molybdenum or tungsten ceramals. This coating consists of several phases, which vary in concentration with distance from the oxidation interface.

All the coatings contained titanium dioxide TiO2. The presence of tungsten trioxide WO3 was detected in the tungsten ceramals, and some molybdenum trioxide MoO3 was present in the molybdenum ceramals. In the cobalt ceramals, cobaltous cobaltic oxide CoO·Co2O3 was detected at the oxidation interface and cobalt titanate CoTiO3 was detected in the inner oxide layer.

Molybdenum trioxide MoO₃ sublimes as a volatile oxide between 480° and 840° F (reference 4). This temperature is well below the experimental temperatures and from this consideration alone no protective value would be expected from MoO₃. Another factor indicating that MoO₃ would have little protective value is its specific-molecular-volume ratio of 3.4. The specific-molecular-volume ratio is the ratio of the specific molecular volume of the oxide to that of the metal. The specific-molecular-volume ratio of WO₃ is also 3.4 and it is well established that the oxide formed on metallic tungsten does not protect the metal from further oxidation (references 5 and 6). The melting point of WO₃ is 2650° F and some evaporation of a WO₃ coating will take place at 1470° F (reference 7). It has been reported that WO₃ sinters at 1650° F (reference 7). The commonly formed oxide of cobalt, cobaltous oxide CoO melts at 3515° F and melting this oxide in air at atmospheric pressure is not accompanied by great amounts of volatilization.

The two factors, low volatization temperature of the oxide and high specific volume of the oxide, would both indicate that the oxide coating formed on molybdenum ceramals would have little protective value. As the MoO3 forms it expands and breaks away from the body at the oxidation interface also fracturing the titanium carbide TiC as well as any TiO2 formed upon oxidation of the TiC. The MoO3 then volatilizes and diffuses to the surface leaving a loosely packed porous coating that has practically no resistance to the diffusion of oxygen. This view of the mechanism of oxidation of the molybdenum ceramals is substantiated by the curves plotted in figure 1, which indicate that the oxidation increase with time occurs as a straight line on rectangular coordinates.

A plot of the depth of oxide formed on the tungsten ceramals against time on semilogarithmic coordinate paper is presented in figure 4(d). The oxide layer formed has some protective action but not as much as would be expected if a dense, homogeneous oxide were formed. This result may be expected, considering that the WO3 formed will break away from the oxidation interface, carrying the TiO2 formed and any TiC remaining; but because the WO3 has a low vapor pressure, the coating will not volatilize and at the two higher test temperatures some sintering of the oxide may have occurred. The building up of the oxide layer, even a rather broken layer, will afford some resistance to oxidation diffusion especially if the oxide coating is partly sintered.

Comparison of figures 6(d) and 4(d) indicates that the oxide penetration of the cobalt ceramals proceeds at approximately the same rate as for the tungsten ceramals at 1785° and 2000° F. At 1625° F, the 5- and 10-percent-tungsten ceramals have better oxidation resistance than the 5- and 10-percent-cobalt ceramals. The molybdenum ceramals are in all cases inferior to the cobalt and tungsten ceramals.

The type of oxide formed on a 30-percent-molybdenum specimen oxidized at 1785° F for 7 hours is shown in figure 8. The line of demarcation between the oxide and the ceramal is even and easily distinguished. If molybdenum is added to the ceramal in amounts that exceed the solubility of molybdenum in titanium carbide, the excess molybdenum will form a grain-boundary layer surrounding the titanium-carbide grains. The formation of such a grain-boundary area could produce a more rapid penetration of the oxidation reaction along the grain boundaries. In the 30-percent-molybdenum ceramal (fig. 9), the grain boundary does not appear to contain an appreciable quantity of a grain-boundary phase and the photomicrograph of the unetched oxidation interface of the same material (fig. 10) shows that the oxidation proceeds as a linear front without marked grain-boundary penetration.

In examining the temperature dependence of the oxidation-rate constant of the molybdenum ceramals (fig. 2), it is evident that the oxidation rate of the 20- and 30-percent-molybdenum ceramals at 1625° F is lower than would be expected if the oxidation mechanism remained unchanged. A possible explanation of the low oxidation rates may be brought out by examination of the photomicrograph of figure 11. The line following the contour of the oxidation interface may mark the vaporization interface of the MoO₃. This line was also found within the oxide layer of the 10-percent molybdenum ceramal oxidized at 1625° F but was not visible on the 20- and 30-percent-molybdenum ceramals oxidized at 1625° F. If the assumption is made

that the line is invisible in the oxide coating of the 20- and 30-percent-molybdenum ceramal oxidized at 1625° F because the increased quantity of MoO_3 results in the extension of the MoO_3 layer to the outer surface of the oxide layer, the low oxidation rate in these two cases may be explained. The thicker MoO_3 layer would result in slower diffusion of oxygen inward and slower oxidation. At high temperatures, the faster sublimation of the MoO_3 would minimize this protective action.

The type of oxidation penetration encountered in the tungsten ceramals is illustrated in figure 12. The penetration is regular and the line of demarcation is even. The oxide coating had a yellow-orange color and was easily distinguished from the gray metallic ceramal. Oxide coatings formed on 5- and 10-percenttungsten ceramals in a series of striations (fig. 13). When the ceramals contained 20 or 30 percent of tungsten, the oxide formed was a homogeneous layer with no striations (fig. 12). The appearances of striated coatings on the ceramals of low tungsten content can be explained by consideration of the specific molecular volume of the oxide formed and the tenacity of the oxide. With low tungsten content, the expanding force of the WOz formed is not great enough to break the oxide from the body until a critical thickness of oxide forms. With 20-percent or more tungsten, the volume of WO3 formed is sufficient to break the TiO2 and WO3 away as fast as they form. In figure 5, the variation in oxidation-rate constant with temperature does not conform with the normal exponential curve. At 2000° F, the oxidation-rate constants of the tungsten ceramals are of approximately the same magnitude. The oxidation-rate constants for the 20- and 30-percent tungsten ceramals at 1785° F are less than at 1625° F, whereas at these temperatures the oxidation-rate constants of the 5- and 10-percent-tungsten ceramals remain practically unchanged.

Several possible factors are available to help explain the anomalous oxidation behavior of the tungsten ceramals. The oxide WO3 undergoes transformation between 1560° and 1650° F (reference 8). This transformation results in a noticeable decrease in oxidation rate at temperatures above the transformation range because of a decrease in solubility of oxygen in the new phase (reference 8). The lowest experimental temperature considered herein is 1625° F, which is within the temperature range suggested. A change in oxygen solubility in WO3 would result in a change in oxidation-rate constant not in keeping with the exponential formula. A further explanation of the wide deviation at 1625° F may be a change in the actual oxidation-penetration mechanism into the body as the percentage of tungsten is increased. Figures 14 and 15

show an unetched and an etched oxidation interface, respectively, for a 30-percent-tungsten specimen. The unetched field shows that the region of the oxidation moves into the ceramal by following paths into the ceramal rather than moving as a linear front. The etched field clearly shows that the paths being followed by the oxide penetration are the grain boundaries. Mention has previously been made that the grain-boundary phase, which forms when the solubility of the metallic element in the titanium carbide is exceeded, does not occur in the 30-percent-molybdenum ceramal. The 20-percent-tungsten ceramal, however, has a wide grain-boundary phase and the amount of this phase visible in the 10-percent-tungsten ceramal is much less.

The oxidation penetration along grain boundaries of the 10-percent-tungsten ceramal is comparatively insignificant, as shown by figure 16. When the oxidation proceeds by grain-boundary penetration, the area of oxidation interface is greatly increased and the total oxidation rate is much more rapid. At 2000° F, the oxidation of the titanium carbide is more rapid and this effect coupled with the decreased solubility of oxygen in the WOz results in a change back from the grain-boundary type of oxidation to a linear oxidation boundary (fig. 17). This change is responsible for the oxidation-rate constants of the ceramals containing high percentages of tungsten at high temperature being of the same order of magnitude. The presence of striations in the oxides of the 5- and 10-percenttungsten ceramals may also have an effect on the oxidation rate of these ceramals. The layers have a greater resistance to oxygen diffusion while they are building up to a critical thickness than would be encountered if the oxide was torn away from the oxidation interface as soon as it formed, as is the case with the ceramals of higher tungsten content. No attempt was made to determine the relative importance of the three changes in oxidation mechanism described, phase change, striated coating, and grain-boundary oxidation. All three changes would tend to produce the deviations shown in the curves of figure 4(d).

The oxide coating that forms on the cobalt ceramals is very tightly adherent and dense. In preparing the specimens of cobalt ceramals for examination after oxidation, it was found that the oxide ground to a metallic-like surface, which made it difficult to determine when the scale was completely removed. The oxide appeared to be less amenable to grinding than the ceramal itself because the removed oxides adhered to the diamond grinding wheel. At a magnification of 50 diameters (fig. 18), the coating appears as two separate layers with transition zones at the oxidation interface and between the layers. During the grinding of several specimens, the scale fractured

along the transition zone between the two layers and the inner layer was observed to have a characteristic green color. This inner layer appeared to be hard, dense, and tightly adhering to the ceramal. No evidence of separation at the oxidation interface was found. In regard to deterioration or loss of cross-sectional area by oxidation, this inner oxide layer can be considered an integral part of the ceramal. As previously mentioned, the coatings on the molybdenum and tungsten ceramals are not tightly adherent and are readily removable.

No significant change in the oxidation-rate constants of the cobalt ceramals is evident at the temperatures considered, excepting the 30-percent-cobalt ceramal at 1625° F, which has a value higher than any of the other temperature-composition combinations (fig. 7). Metallographic study of these coatings did not reveal any explanation for the abnormality of the 30-percent-cobalt ceramal. None of these ceramals show any sign of intergranular oxide penetration and in all cases the scales appear similar. The photomicrograph (fig. 19) shows that the oxidation mechanism of cobalt ceramals is not as simple as that of the tungsten and molybdenum ceramals. At the oxidation interface, a thin layer of material forms that is probably a transition zone containing the partly oxidized ceramal material and the oxidation products first formed. Near this layer, the scale is a two-phase material with light insular particles in a darker matrix. Farther from the oxidation interface, the light phase rather suddenly disappears leaving only the dark phase near the outer surface. Examination by X-ray diffraction indicated the presence of CoO.Co.203 close to the oxidation interface and CoTiO3 at the outer face of the inner layer of scale. When the oxide chipped off during grinding, the fracture occurred just inward from the area in which the last of the light phase finally disappears. Only TiO2 was found to be definitely present in the outer dark layer. Apparently the CoO.Co203 and a portion of the TiO2 that forms at the oxidation interface combine to form CoTiO3 and the CoTiO3 enters into solution in the TiO2. The behavior during oxidation of the 30-percent-cobalt material is probably the result of the complex reactions taking place throughout the oxygen-diffusion zone and of the effect variations in temperature and concentration of cobalt may have on these reactions.

Of the compositions considered, the use of cobalt, tungsten, and molybdenum as metallic additions will result in a marked difference in oxidation resistance. With regard to oxidation, the tungsten compositions are superior to the molybdenum compositions and the cobalt compositions are in general superior to both.

The maximum percentage of cobalt that may be added without a drastic increase in oxidation penetration at 1625° F is apparently between 20 and 30 percent. At temperatures in the vicinity of 2000° F, the use of 30-percent cobalt will not result in much more oxidation than would be encountered with 20 percent of cobalt. The critical composition of tungsten ceramal at 1625° F is between 10 and 20 percent of tungsten with the 20-percent-tungsten ceramal showing a marked increase in oxidation penetration. At higher temperatures, no sudden change in oxidation-rate constant with change in temperature is noted. The oxidation-rate constants of the 20-and 30-percent-tungsten ceramals at 2000° F are approximately equal.

The resistance to oxidation of ceramals within the range of compositions and temperatures investigated may be determined by using figures l(a), 4(d), and 6(d). By interpolation, the oxidation penetration to be expected as a result of exposure at temperatures from 1625° to 2000° F and with a variation in metallic composition up to 30 percent can be estimated.

These results make it clear that before the high melting points and the high-temperature properties of metallic molybdenum, tungsten, and cobalt can be used to advantage in air atmospheres, protection of these metals will be necessary either by use of coatings applied to the exterior or by use of additional components in the ceramal itself that will combine chemically with the oxygen or with the oxides formed into a dense material highly resistant to the diffusion of oxygen. The cobalt ceramal shows promise because of the type of oxide coating formed. This coating forms in two layers with the inner layer occurring as a composite of the body and oxides, with a gradual change in composition moving outward from the inner interface.

SUMMARY OF RESULTS

The following results were obtained from an investigation conducted to determine the oxidation-penetration characteristics of tungsten carbide base ceramals containing 5, 10, 20, and 30 percent of molybdenum, tungsten, or cobalt at various temperatures and exposure periods:

- 1. The oxidation resistance in air atmospheres at 1625°, 1785°, and 2000° F of molybdenum, tungsten, and cobalt titanium carbide base ceramals was found to vary in the following manner:
 - (a) The depth of oxide penetration for the cobalt and tungsten ceramals was approximately the same through the time

and temperature range investigated. The cobalt ceramals were considered better with regard to over-all oxidation because of the type of oxide coating formed.

- (b) At 1625° F, the 20- and 30-percent-tungsten ceramals oxidized much more rapidly than the 5- and 10-percent-tungsten ceramals. At 2000° F, the oxidation-penetration rates of the tungsten ceramals were of the same order of magnitude.
- (c) The molybdenum ceramals were inferior to both the cobalt and the tungsten ceramals in oxidation resistance, showing no self-protective properties. The oxide coatings formed on the molybdenum ceramals did not inhibit further oxidation. Their oxidation rates increased greatly as temperature increased and as the percentage of molybdenum was increased. At 1625° F, the oxidation rates of the 20- and 30-percent-molybdenum ceramals were lower than would be expected from the rates of the other compositions.
- 2. The oxidation-penetration time curves may be used to estimate the expected depths of oxidation penetration through the temperature range of 1625° to 2000° F and 5- to 30-percent metallic element.

CONCLUSION

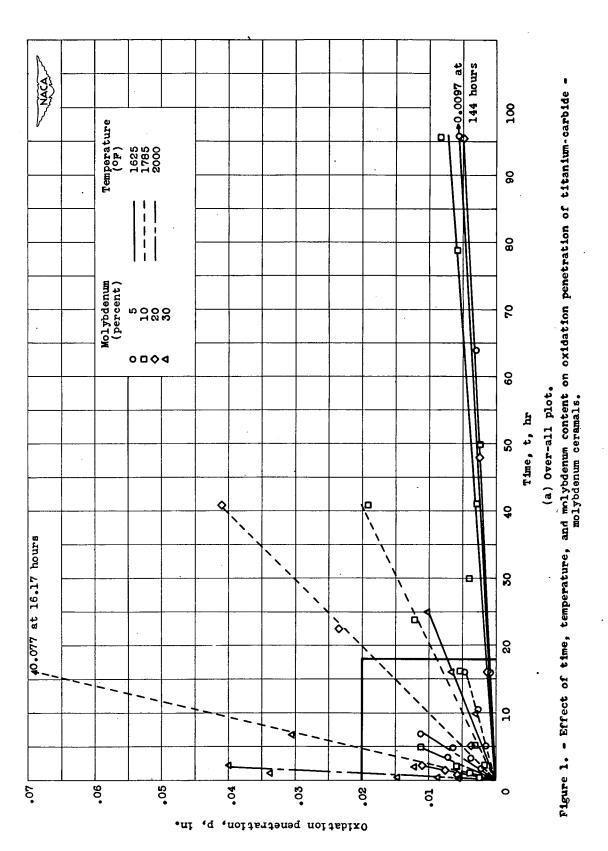
Combined with data on the effect of the metallic components on the strength properties of the ceramals, the oxidation-penetration curves and the oxidation-rate constant plotted against the reciprocal of absolute temperature can be used in deciding the optimum percentage of alloying metallic element to add to a titanium carbide body for the highest strength within the allowable oxidation-rate limit.

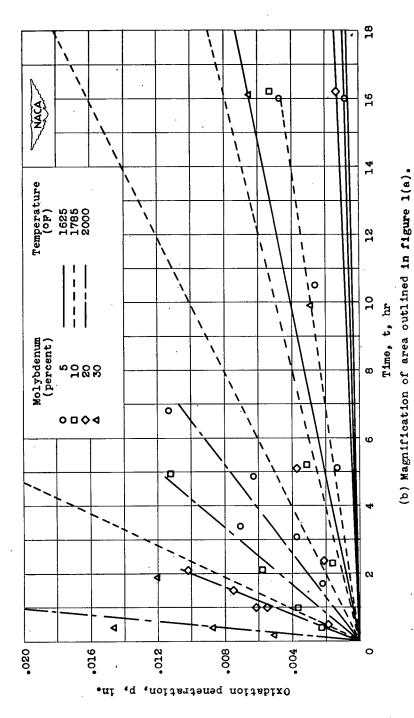
Lewis Flight Propulsion Laboratory, National Advisory Committee for Aeronautics, Cleveland, Ohio, February 11, 1949.

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Effect of time, temperature, and molybdenum content on oxidation penetration of titanium carbide - molybdenum ceramals. Figure 1. - Concluded.

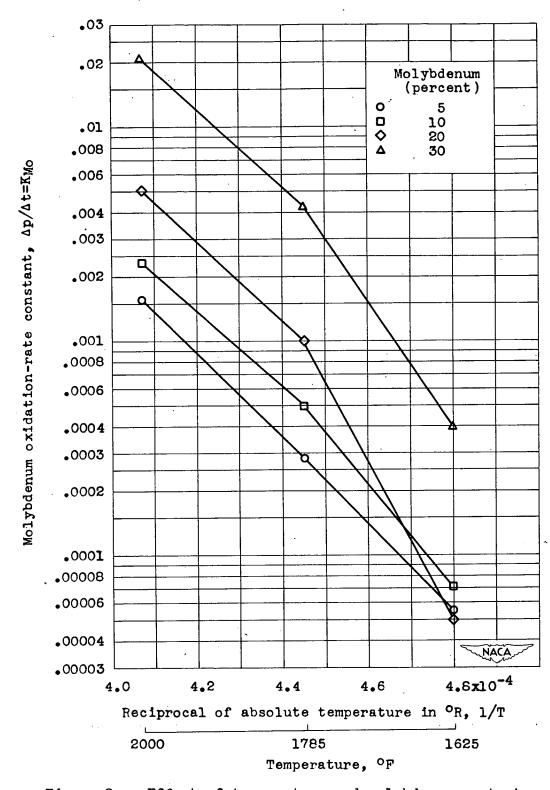


Figure 2. - Effect of temperature and molybdenum content on oxidation-rate constant of titanium carbide - molybdenum ceramals.

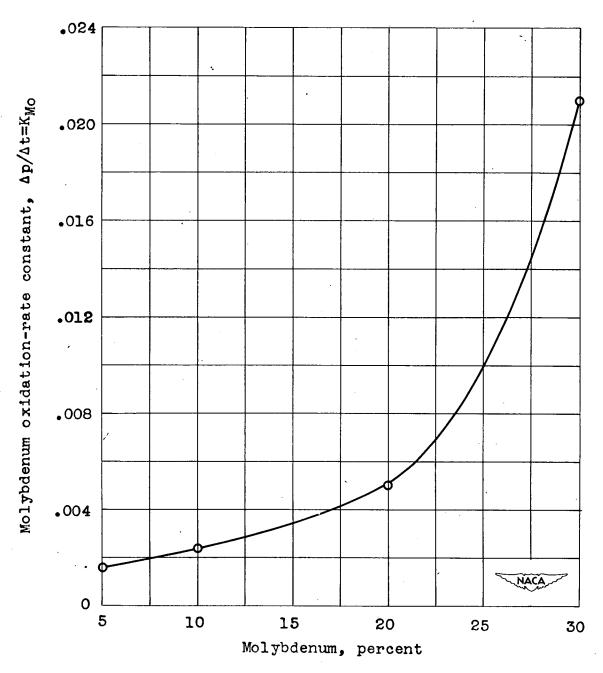
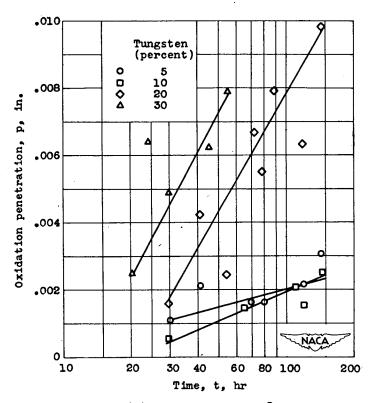


Figure 3. - Effect of molybdenum content on oxidation-rate constant at 2000° F for titanium carbide - molybdenum ceramals.



(a) Temperature, 1625° F.

Figure 4. - Effect of time, temperature, and tungsten content on oxidation penetration of titanium carbide - tungsten ceramals.

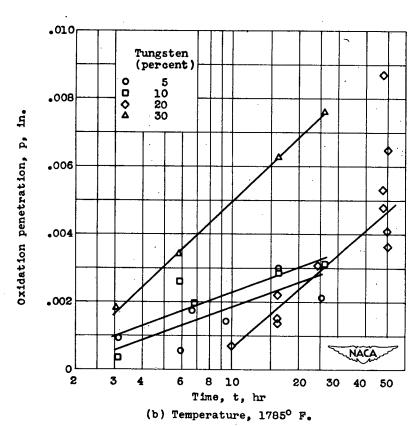


Figure 4. - Continued. Effect of time, temperature, and tungsten content on oxidation penetration of titanium carbide - tungsten ceramals.

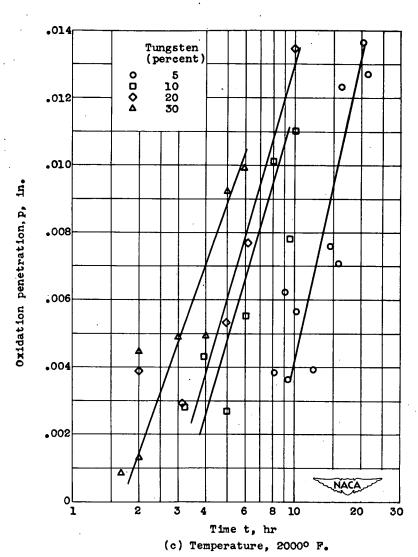


Figure 4. - Continued. Effect of time, temperature, and tungsten content on oxidation penetration of titanium carbide - tungsten ceramals.

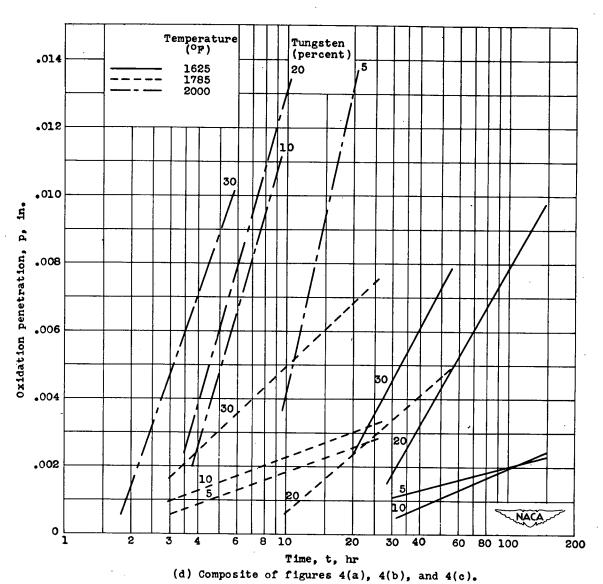


Figure 4. - Concluded. Effect of time, temperature, and tungsten content on oxidation penetration of titanium carbide - tungsten ceramals.

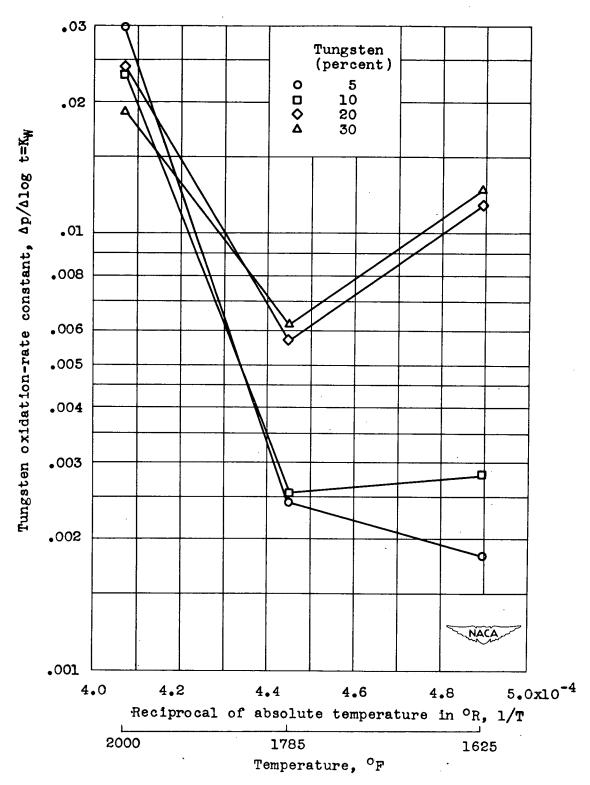
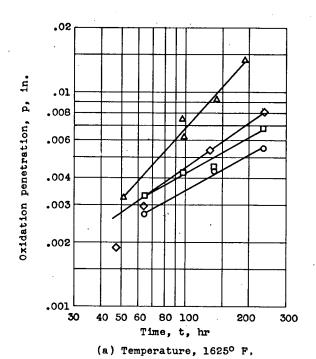


Figure 5. - Effect of temperature and tungsten content on oxidation-rate constant of titanium carbide - tungsten ceramals.



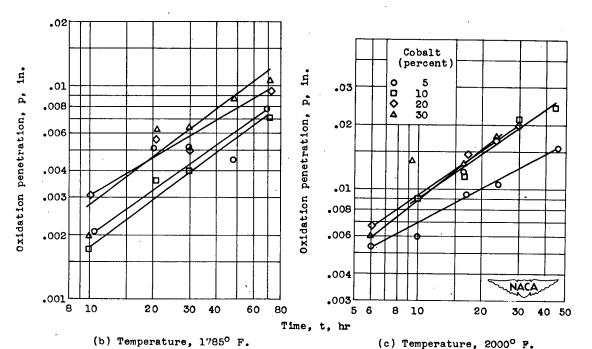
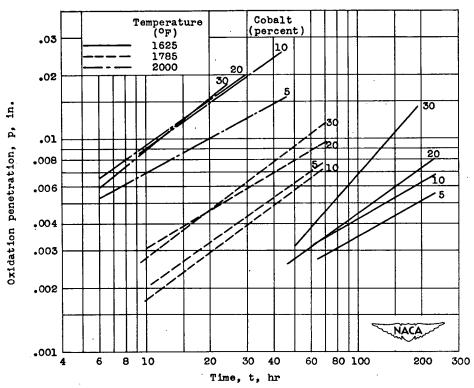


Figure 6. - Effect of time, temperature, and cobalt content on oxidation penetration of titanium carbide - cobalt ceramals.



(d) Composite of figures 6(a), 6(b), and 6(c).

Figure 6. - Concluded. Effect of time, temperature, and cobalt content on oxidation penetration of titanium carbide - cobalt ceramals.

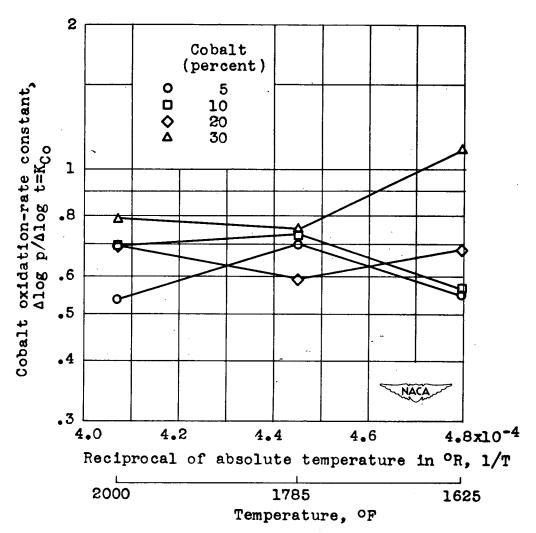


Figure 7. - Effect of temperature and cobalt content on oxidation-rate constant of titanium carbide - cobalt ceramals.

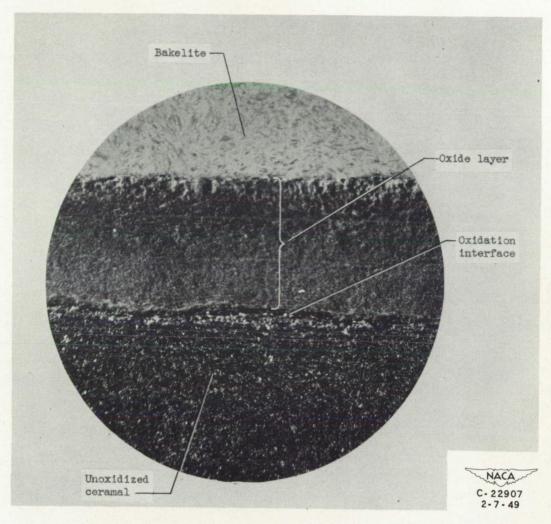


Figure 8. - Oxidation of 30-percent-molybdenum - titanium carbide ceramal. Temperature, 1785° F; time at temperature, 7 hours; unetched; magnification X50.

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Figure 9. - Region adjacent to oxidation interface of 30-percent-molybdenum — titanium carbide ceramal. Grain boundary does not appear to contain appreciable quantity of grain-boundary phase. Temperature, 1785° F; time at temperature, 7 hours; etchant, potassium hydroxide plus potassium ferricyanide KOH+K3Fe(CN)6; magnification, X1000.

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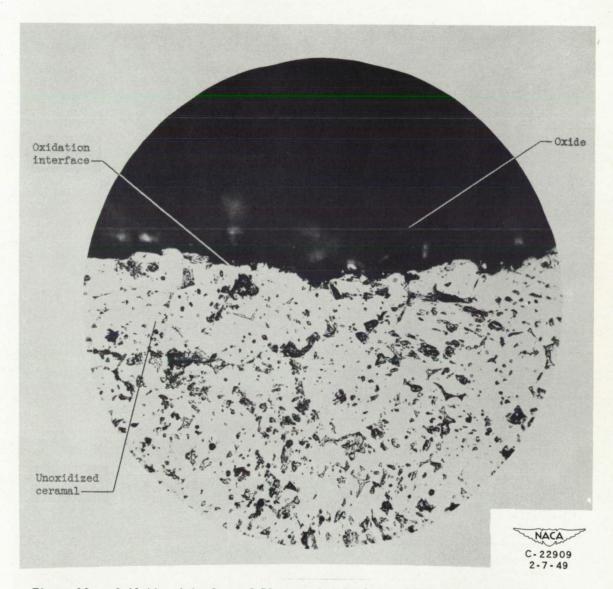


Figure 10. - Oxidation interface of 30-percent-molybdenum - titanium carbide ceramal. Oxidation proceeds as linear front without grain-boundary penetration. Temperature, 1785° F; time at temperature, 7 hours; etchant, potassium hydroxide plus potassium ferricyanide KOH+K₃Fe(CN)₆; magnification, X500.

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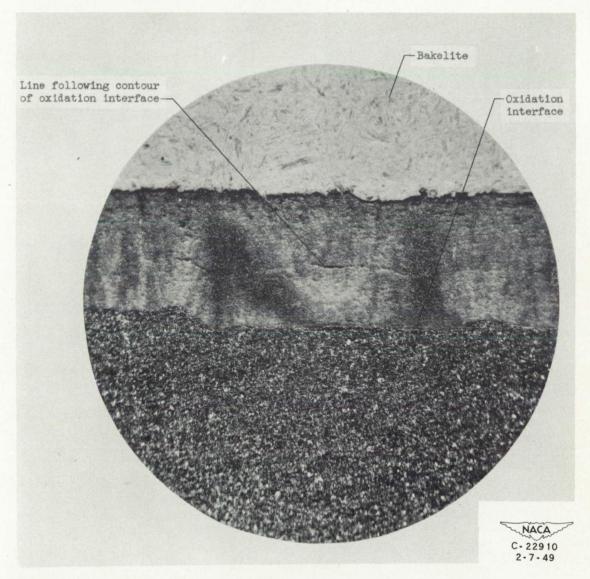


Figure 11. - Oxidation zone of 10-percent-molybdenum - titanium carbide ceramal. Line within oxide coating follows contour of oxidation interface. Temperature, 1785° F; time at temperature, 40 hours; unetched; magnification, X50.

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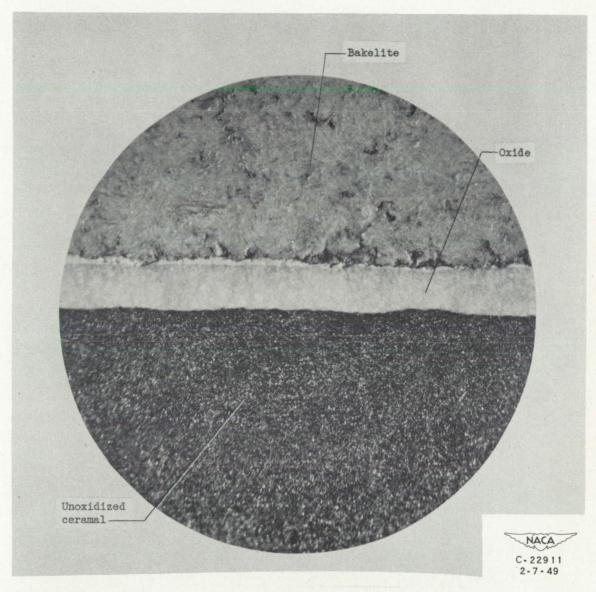


Figure 12. - Oxidation zone of 30-percent-tungsten - titanium carbide ceramal. Under low magnification oxide penetration is regular and line of demarcation between oxide and ceramal is even. Temperature, 1785° F; time at temperature, 30 hours; unetched; magnification, X50.

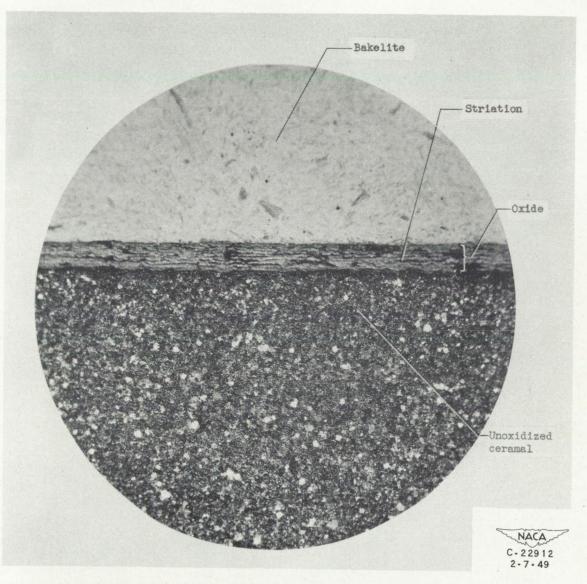


Figure 13. - Oxidation zone of 10-percent-tungsten - titanium carbide ceramal. Striations appear in oxide coatings of 5- and 10-percent-tungsten ceramals. Temperature, 1785° F; time at temperature, 30 hours; unetched; magnification, X50.

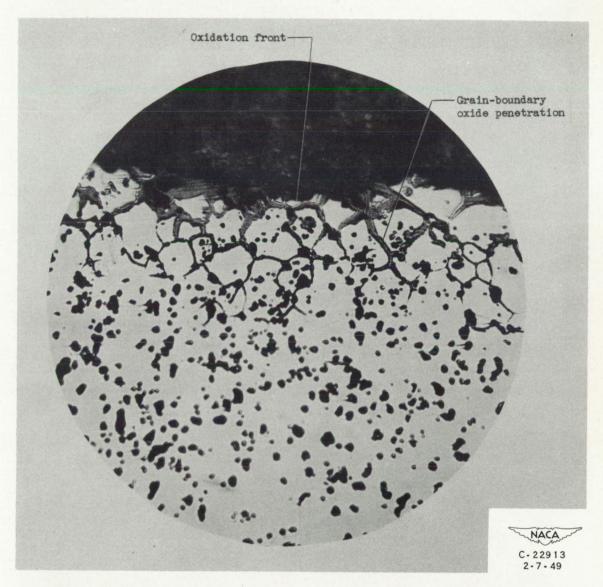


Figure 14. - Oxidation interface of 30-percent-tungsten - titanium carbide ceramal. Oxidation proceeds along grain boundaries rather than moving as linear front. Temperature, 1785° F; time at temperature, 30 hours; unetched; magnification, X750.

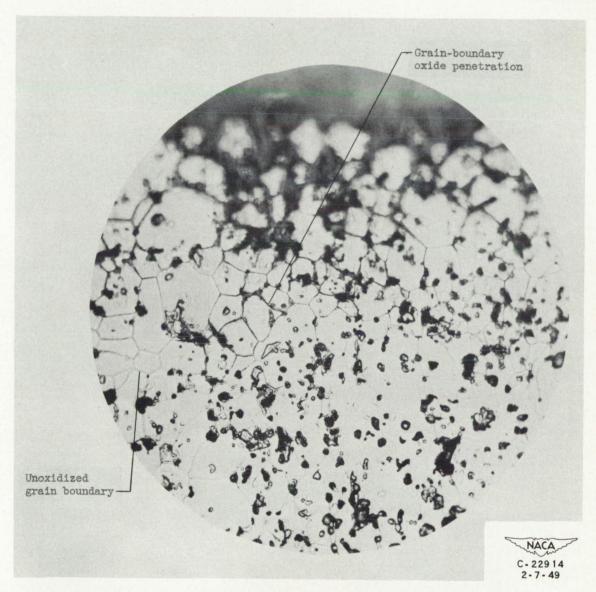


Figure 15. - Grain-boundary oxide penetration into 30-percent-tungsten - titanium carbide ceramal. Temperature, 1785° F; time at temperature, 30 hours; etchant, potassium hydroxide plus potassium ferricyanide KOH+K₃Fe(CN)₆; magnification, X750.

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Figure 16. - Oxidation interface of 10-percent-tungsten - titanium carbide ceramal. No preferential oxide penetration along grain boundaries is visible. Temperature, 1785° F; time at temperature, 30 hours; etchant, potassium hydroxide plus potassium ferricyanide KOH+K₃Fe(CN)₆; magnification, X750.

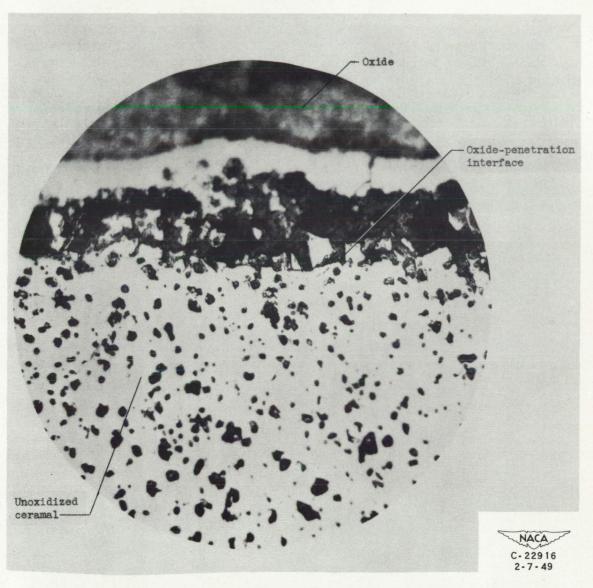


Figure 17. - Oxidation interface of 30-percent-tungsten - titanium carbide ceramal. Oxidation progresses as linear front and grain-boundary oxide penetration is inappreciable. Temperature, 2000° F; time at temperature, 4 hours; unetched; magnification, X750.

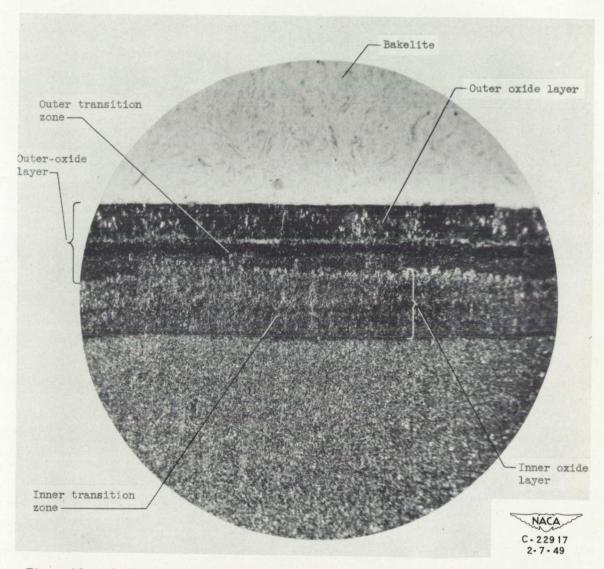


Figure 18. - Oxidation zone of 30-percent-cobalt - titanium carbide ceramal. Oxide coating appears as two layers separated at oxidation interface and between layers by transition zone. Temperature, 2000° F; time at temperature, 30 hours; unetched; magnification, X50.

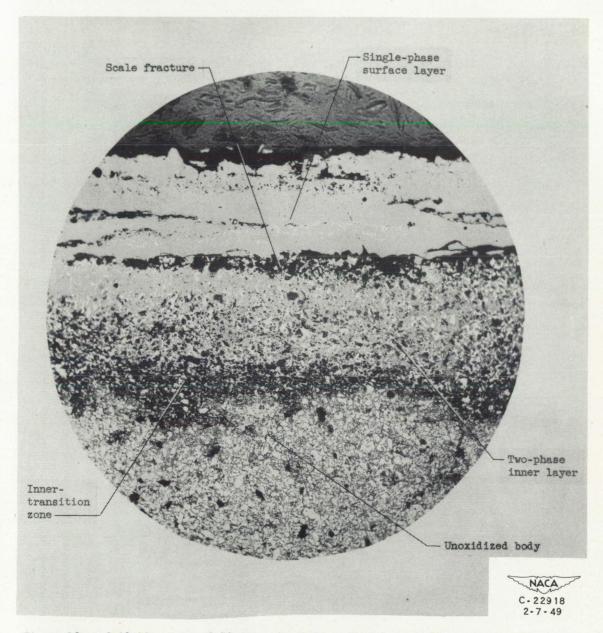


Figure 19. - Oxidation zone of 30-percent-cobalt — titanium carbide ceramal. This view illustrates complex nature of oxide coatings found on cobalt-bearing ceramals. Temperature, 1625° F; time at temperature, 100 hours; etchant, potassium hydroxide plus potassium ferricyanide KOH+K₃Fe(CN)₆; magnification, X250.